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Journal of Polymer Science, Part B

Polymer Letters

Editorial Board: R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

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Journal of Polymer Science **Part B: Polymer Letters**

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POLYMER LETTERS VOL. 1, PP. 529-530 (1963)

INFRARED SPECTRA OF POLYETHYLENE OXYBENZOATE

The molecular structure of poly-p-ethylene oxybenzoate, $(-C_6H_4 \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot O-)_n$, (PEOB), is similar to that of polyethylene terephthalate, $(-C_6H_4CO \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot CO-)_n$, (PETP).

As with PETP, a glassy, noncrystalline specimen of PEOB is obtained by quenching from the melt. A fairly crystalline specimen is obtained by heating the noncrystalline specimen at 100°C. or higher temperatures for several hours. An oriented, crystalline specimen is obtained by drawing the noncrystalline or the crystalline specimen at room or higher temperatures. X-ray diffraction pattern and infrared spectrum of PEOB are affected by both crystallization and drawing. These changes are made clear as follows with the aid of the previous data (1-8) from PETP and benzene.

The absorption bands at 2952 and 2880 cm.$^{-1}$ can be assigned to the CH_2 antisymmetric stretching ($\nu_a(CH_2)$) and to the CH_2 symmetric stretching ($\nu_s(CH_2)$) modes, respectively, on the basis of their well-known positions in hydrocarbons. Both of these bands show the σ-polarization. The band positions do not change appreciably by crystallization. On the other hand these stretching bands in PETP show the π-polarization which is inconsistent with the σ-polarization predicted from the crystal structure (9). These bands in PETP are found at 2960 and 2888 cm.$^{-1}$ in the noncrystalline specimen and shift to 2968 and 2903 cm.$^{-1}$ in the crystalline one.

The 1723 cm.$^{-1}$ band assigned to C=O stretching (ν(C=O)) mode in PETP is found at 1712 cm.$^{-1}$ in PEOB. Corresponding with the band position of the (ν(C=O)) mode, the band at 3432 cm.$^{-1}$ assigned to the overtone of the (ν(C=O)) mode in PETP comes out at 3407 cm.$^{-1}$ in PEOB.

The intensity of the 1608, 1583, 1372, 1169, 1106, 697, 630, and 515 cm.$^{-1}$ bands in PEOB does not exhibit appreciable change by crystallization, though the corresponding bands in PETP at 1616, 1580, 1370, 1173, 1102, 680, 631, and 509 cm.$^{-1}$ show a marked decrease of intensity. The 1370 and 1173 cm.$^{-1}$ bands in PETP have been assigned to the CH_2 wagging ($\gamma_w(CH_2)$) (3-5,7), and to the CH_2 twisting ($\gamma_t(CH_2)$) (5), modes of the $-O \cdot CH_2 \cdot CH_2 \cdot O-$ groups in the noncrystalline regions, respectively.

Liang and Krimm (6) have suggested that the bands whose intensity decreases with an increase in crystalline content of PETP originate

$$-C \cdot C_6H_4 \cdot C-$$
(O on each C)

from the loss of the symmetry of the $-C \cdot C_6H_4 \cdot C-$ portion in the noncrystalline region.

It should be reasonable to analogize from the suggestion (6) for PETP

$$-O\cdot C_6H_4\cdot\overset{\overset{O}{\|}}{C}-$$

and from the chemical structure of PEOB that the $-O\cdot C_6H_4\cdot\overset{\overset{O}{\|}}{C}-$ groups in PEOB do not possess the center of the symmetry not only in the noncrystalline phase, but also in the crystalline phase.

The bands at 1370 and 1173 cm.$^{-1}$ in PETP, therefore, may not be

$$-\overset{\overset{O}{\|}}{C}\cdot C_6H_4\cdot\overset{\overset{O}{\|}}{C}-$$

the CH_2 modes but result from the $-\overset{\overset{O}{\|}}{C}\cdot C_6H_4\cdot\overset{\overset{O}{\|}}{C}-$ units in the noncrystalline phase.

It should be stated from the infrared result of PEOB that the "amorphous" bands in PETP are associated with the relaxation of the symmetry of the $-\overset{\overset{O}{\|}}{C}\cdot C_6H_4\cdot\overset{\overset{O}{\|}}{C}-$ units in the noncrystalline region.

The complete assignment of the spectra of PETP and PEOB must await further work on the structure of PEOB, and on the infrared spectra of the various, deuterated PEOB and the related compounds.

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SINGLE CRYSTALS OF POLYVINYL ALCOHOL

It is well known that many polymers crystallize in a lamellar state when their melts or solutions are cooled, and that they form definite shaped single crystals when crystallized slowly from dilute solutions (1). It has not yet been recognized, however, that polyvinyl alcohol (PVA) crystallizes as single crystals or spherulites. Recently, the authors (2) and Hirai et al. (3) succeeded independently in obtaining PVA single crystals.

Figures 1 and 2 are electron micrographs of the single crystals of PVA. The platelets are parallelogrammic in shape. In many cases the ratio of the length of the longer side to the shorter side is fairly constant and is about 5. The lamella thickness estimated from the length of the shadow is 100–150 A. The acute angle of the parallelogram is about 55°. Another characteristic feature is the occurrence of corrugations inclined at 20° – 30° to the longer side of the platelet. The presence of such corrugations on the single crystals suggests that the lamellae did not grow as a flat layer, but as a semidome or a corrugated platelet during the crystallization. The corrugations could result from slip or gradual deformation along certain crystallographic planes. Such an interpretation was also made for the corrugations occurring on polyethylene single crystals (1,4). Many small particles are observed which adhered mainly to the longer side of the platelets, but their nature is not yet clear.

A selected-area electron diffraction pattern of a PVA single crystal is shown in Figure 3. The spacings and the intensities of the reflections nearly correspond to those of the x-ray reflections of PVA fibers (5). The four stronger spots correspond to the reflections of the $(10\bar{1})$ and (101) planes and the weaker spots to those of the (200) plane. Fur-

Fig. 1. Electron micrograph of PVA single crystals.

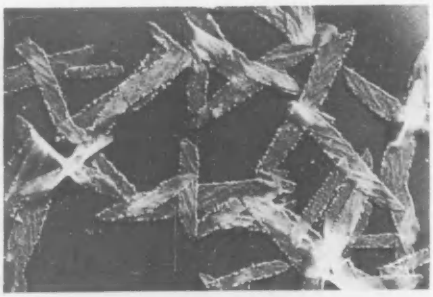

Fig. 2. Electron micrograph of PVA single crystals.

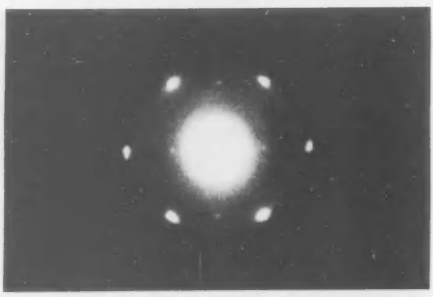

Fig. 3. Selected-area electron diffraction pattern from a crystal of PVA, shorter side of the parallelogram is vertical.

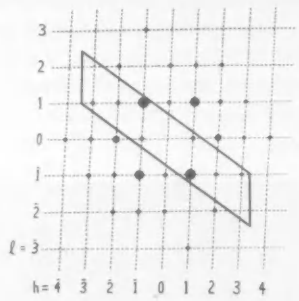

Fig. 4. Reflections and reciprocal lattice diagram. Dots show observed position of reflections. Heavy lines represent external form of a single crystal, dotted lines reciprocal lattice of a* c* planes.

ther, many other spots corresponding to the (h0l) planes of the PVA crystal are observed in the original negative plate, though they are hardly seen in Figure 3. Indices of the observed spots are shown in Figure

4. As all of the spots correspond to equatorial reflections in x-ray diffraction of PVA fibers, it can be concluded that the chain axes (b-axis) are normal to the lamellae. Since the thickness of the single crystals is 100 – 150 A., the molecules are much longer than the thickness of the platelet. Therefore, the molecules must fold back and forth in some way through the platelet. From the correlation of the electron micrograph and the electron diffraction pattern, it is concluded that the longer side of the parallelogram corresponds to the (101) plane and the shorter side to the (100) plane. The observed value of about 55° for the acute angle is nearly equal to the calculated angle between the (100) and (101) planes. The direction of the corrugations corresponds to the (301) or (201) plane.

From electron diffraction of a single crystal of PVA cast with Pd or Al, the cell constants can be precisely determined as $a = 7.81 \pm 0.02$ A., $c = 5.43 \pm 0.01$ A., and $\beta = 91° 30' \pm 15'$. In this case reflections both from PVA and Pd or Al are simultaneously photographed in the same plate. The length of the c-axis obtained from the electron diffraction of the single crystal is slightly shorter than those from x-ray diffraction of PVA fibers (5-7).

Among the usual crystals of parallelogrammic shape, there are L-shaped platelet with an angle of about 140° and lath-shaped lamella as shown in Figure 2. From the shape of the crystals and the pattern of the corrugations on it, it seems likely that these are twinned crystals, that is, two lamellae joined upon one common face. The twin face of the lath-shaped crystal is the (101) plane and that of L-shaped crystal is the $(10\bar{1})$ plane. The characteristic behaviors of the (101) and $(10\bar{1})$ planes in the PVA crystals were also recognized in the studies of films and fibers by x-ray diffraction (8).

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NOTE ON THE THERMAL DEGRADATION OF TEFLON

In connection with studies carried out in these laboratories on the thermal degradation of polymers in vacuo, several experiments were performed on Teflon, under both conditions of constant heating rate and at constant temperature. There has been controversy in the literature (1-3) concerning the kinetic order of degradation of Teflon at relatively low temperatures (<500°C.) and this point was examined by the above two series of experiments. In addition, the data were analyzed by heretofore, to our knowledge, unreported methods.

The Teflon 7 used was obtained from DuPont. An American Instrument Company thermogravimetric balance with continuous recording was used. Powdered samples of up to 200 mg. were used. The vacuum was 1 mm. Hg or less for all of the experiments.

In the experiments at constant heating rate, the reaction rates were obtained from the primary thermograms by graphical differentiation. In order to evaluate the kinetics of degradation, the method of Freeman (4) was used initially. This method employs the expression,

$$\Delta \log R_t = n \Delta \log W_r - (E/2.303R) \Delta (1/T). \qquad (1)$$

where R_t is the rate of reaction, n is the reaction order, E is the activation energy, R is the gas constant, T is absolute temperature, and $W_r = \Delta W_c - \Delta W$, ΔW being weight loss at the point where the rate is taken, and ΔW_c the total weight loss associated with a given reaction.

In order to check this method a procedure involving use of the relation,

$$\log R_t = \log A + (E/R) [(W_M/T_M^2 R_M) \log W - (1/2.303 T)] \qquad (2)$$

was used, where W_M, T_M, and R_M are the weight remaining, temperature, and rate, respectively, at the maximum rate. The activation energy was obtained from the slope of the line obtained by plotting $\log R_t$ versus $[(W_M/T_M^2 R_M) \log W - (1/2.303T)]$. After the activation energy was obtained the order was determined by

$$n = (W_M/T_M^2 R_M) (E/R) \qquad (3)$$

Table I shows results obtained by the two methods. From this table it appears that the activation energy is about the same magnitude as previously reported (2), and that the reaction is first-order over the temperature range investigated.

As indicated in Table II, constant temperature measurements were

TABLE I

Order of Reaction and Activation Energy for Vacuum Thermal Degradation of Teflon (TGA)

Run No.	Heating rate, °C./min.	Order	E, kcal.
	Freeman method		
1	6	1.00	74
2	6	1.03	69
3	3	1.16	74
	From eqs. (2) and (3)		
1	6	1.16	71
2	6	0.93	74
3	3	0.95	71

made at six temperatures. In all cases there was gentle curvature in the weight loss versus time plots, so that zero-order kinetics apparently do not apply. The first-order rate constants, k_1, were evaluated by a simplified method using the relation,

$$k_1 = 2k_0/(2W_0 - k_0t) \tag{4}$$

k_0 being the zero-order rate constant and W_0 the initial weight loss. Since the curvature was gentle, it was assumed that portions of these curves could be approximated as straight lines, k_0 being the slope of the linear portion. Then eq. (4) was used, W_0 being the weight at the beginning of the straight line portion and t the time interval. First-order rate constants determined in this way are compared with those calculated from the relation found by Madorsky et al. (5), i.e.,

$$k_1 = 4.7 \times 10^{18} e^{-80,500/RT} \text{ sec.}^{-1} \tag{5}$$

The limits indicated in Table II for the values from (5) were obtained by considering the temperature range in column 1 of the table. The agreement in k_1 values seems to be reasonably good, indicating that the rapid method proposed in this work is a good approximation.

Our work indicates that the vacuum thermal degradation of Teflon is first-order over the entire temperature range studied. Since the same k_1 values are obtained at various conversions, it also appears that k_1 is independent of the initial molecular weight of Teflon, as has been previously reported (6).

TABLE II

Various Kinetic Parameters for Teflon from Constant Temperature Decomposition Runs

Temp., °C.	Conv., %	Apparent zero-order rate constant, k_0, mg./min.	First-order rate constant, k_1, from eq. (4), min.$^{-1}$	k_1, min.$^{-1}$ from eq. (5)	k_1, min.$^{-1}$ from first-order log plot
473 ± .5	10 – 24	0.046	0.00107	0.00105 ± .00004	–
	24 – 30	0.038	0.00103		
483 ± 1	21 – 50	0.156	0.0024	0.0022 ± .0002	–
	50 – 54	0.090	0.0019		
	54 – 59	0.075	0.0017		
493.5 ± .5	34 – 60	0.21	0.0041	0.0044 ± .0002	–
	60 – 74	0.13	0.0041		
503 ± .5	37 – 50	0.42	0.0074	0.0085 ± .0003	–
	50 – 73	0.30	0.0078		
	73 – 84	0.17	0.0078		
520 ± 1	60 – 67	0.77	0.021	0.025 ± .002	–
	67 – 74	0.56	0.020		
	74 – 84	0.42	0.021		
	84 – 91	0.25	0.021		
533 ± 1	80 – 100			0.060 ± .004	0.056

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POLYMER LETTERS VOL. 1, PP. 539-544 (1963)

RUPTURE BEHAVIOR OF ELASTOMERS: EFFECT OF STATISTICAL VARIABILITY AND CROSSLINK DENSITY

T. L. Smith (1) has recently proposed that rupture data for elastomers be examined in terms of a failure envelope, a plot of log σ_b (T_0/T) versus log ϵ_b. σ_b is the tensile strength based on the original cross-sectional area, (T_0/T) is the usual temperature reduction factor, and ϵ_b is the rupture strain. For materials which obey time-temperature superposition, the shape of the failure envelope is independent of the test rate or temperature, although changes in these variables shift the location of response along the envelope.

We wish to report an investigation of the effects of statistical distribution of break properties on the resolution of the envelope and the effects of changing the crosslink density on its shape and location in the

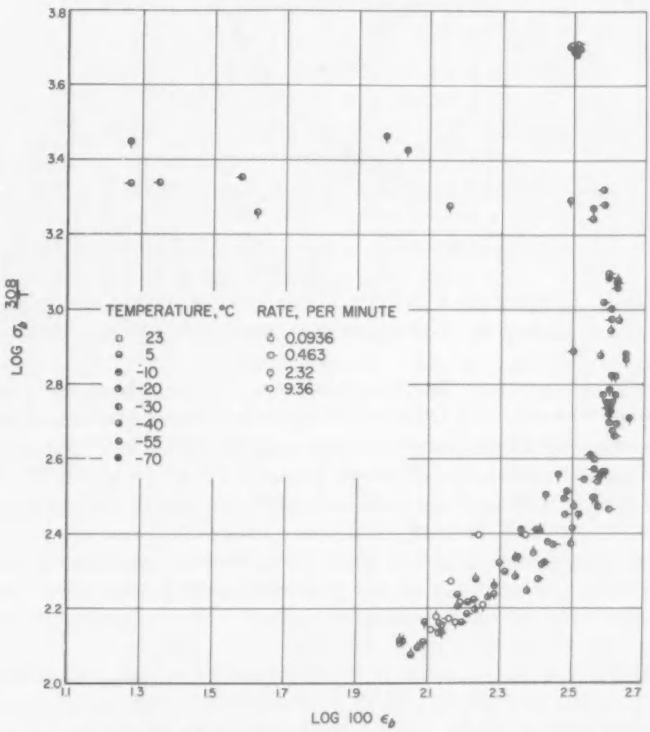

Fig. 1. Failure envelope for a peroxide cured SBR vulcanizate, M_c = 5,500 g./mole.

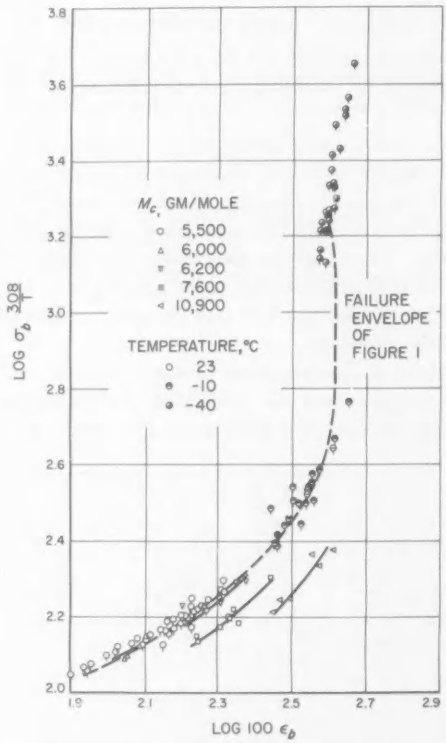

Fig. 2. Effect of crosslink density and statistical variability on the ultimate properties of peroxide cured SBR vulcanizates.

log σ_b, log ϵ_b plane. The tensile failure properties of dicumyl peroxide cured commercial SBR (Philprene 1500) were determined by making measurements on ring samples at four strain rates (0.0936, 0.463, 2.32, and 9.36/min.) and at eight temperatures (23, 5, −10, −20, −30, −40, −55, and −70°C.). These data were used to construct a failure envelope and to check the statistical distribution of breaks.

Statistical Variability. To provide an indication of the statistical variability, an additional 21 samples were tested (at the same time as the first four samples) at the strain rate of 2.32/min. at three temperatures: 23, −10, and −40°C.

Figure 1 shows the failure envelope obtained by varying test rate and temperature. At −55 and −70°C., the samples underwent cold drawing, as previously noted for SBR by Smith, but the points are included for completeness. The presence of a large amount of scatter in this temperature region has already been noted by Smith.

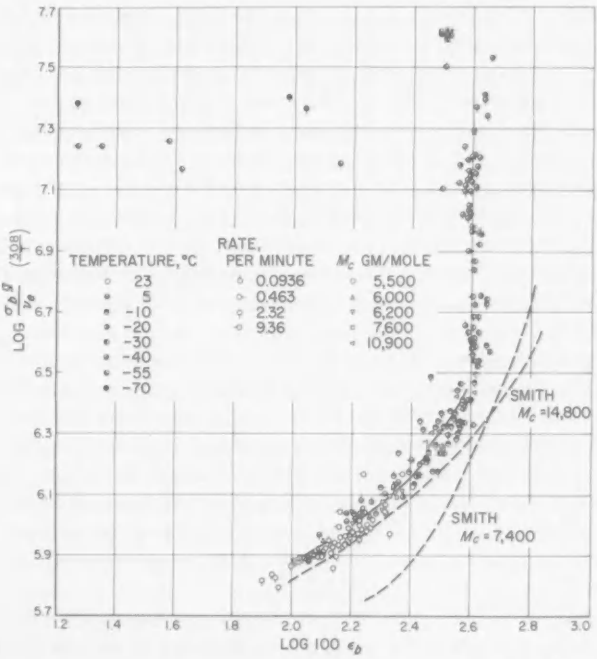

Fig. 3. Reduced failure envelope for the data shown in Figs. 1 and 2.

Figure 2 indicates the envelope of Figure 1 as the dashed line and the individual results from the larger sample populations. At high and intermediate temperatures, the statistically distributed data agree with the average curve obtained from single samples tested at varying rates and temperatures. Thus the stress-strain curves in this region either coincide with or are parallel to the envelope, so the latter can be obtained by breaking a large number of samples at one convenient test rate and one or two temperatures. At low temperatures, when the failure strain begins to decrease, the stress-strain curves, even in the absence of cold drawing, would no longer be parallel to the failure envelope, and the distribution of rupture points would cut across the envelope. Thus, in this region, several samples must be tested at any given rate or temperature in order to define the location of the envelope.

Crosslink Density. Smith (2) has noted that the high temperature end of the failure envelopes of five rubbers differed by a factor equal to the equilibrium modulus; however, the modulus variation was not very great. According to the theory of Bueche and Dudek (3), the tensile strength should vary as (ν_e/g), where g is the gel fraction and ν_e is the concentration of effective chains per gram of whole polymer. Accordingly, we

have tested four other samples of SBR cured to M_c's of 10,900, 7,600, 6,200, and 6,000 g./mole, the value for the first sample being 5,500, all determined by swelling in benzene at 25°C. taking $\mu = 0.34$. Three to six rings from each sheet were tested at a strain rate of 2.32/min. at 23°C., i.e., a portion of the envelope was obtained from statistical variability. These results are also shown in Figure 2. Both failure stress and strain vary with M_c, hence, a new portion of the failure envelope is being scanned, i.e., the area of response in the log σ_b, log ϵ_b plane is shifted to the right as M_c is increased. For M_c values higher than about 10,900, where there is ample evidence that at constant rate and temperature, both breaking stress and strain continue to increase with increasing M_c, one would expect the response to be shifted upward and to the right.

Employing the measured (g/ν_e) factors, the data are re-plotted in Figure 3. The data points for $M_c = 5,500$ from Figures 1 and 2 are also shown. It can be seen that the factor (g/ν_e) superposes the final four samples on the first to within the experimental error of the latter (±5%). Thus the observation of Smith and the prediction of Bueche are confirmed. Note that within certain limits, the effect on the reduced failure envelope of increasing M_c at constant rate and temperature is equivalent to increasing the rate or decreasing the temperature when M_c is held constant.

The complete failure envelopes are curves open toward the log σ_b axis. As M_c increases, the maximum value of log ϵ_b increases. As a result only the lower portions of a series of envelopes representing an increasing M_c can be superposed by use of the factor (g/ν_e). The remainder of the envelope will diverge from the common response at progressively higher values of strain. Thus the strain region at which the envelope has an infinite slope is also a measure of M_c.

As a check, on the (g/ν_e) factor, the published failure envelope data on sulfur cured SBR of Smith (1), reduced by the factor (g/ν_e) were also compared to Figure 3. We took $M_c$values as determined by swelling in benzene and assumed $g = 0.9$. The results for our samples and his of $M_c = 14,800$ are in good agreement, but for some reason his of $M_c = 7,400$ seem to be too low.

As a further check of the prediction, samples of polybutadiene (PBD), Firestone Diene NF 35, were cured with sulfur and mercaptobenzothiazole to M_c values of 7,700, 8,600, and 9,800. These were tested in quadruplicate at a strain rate of 2.32/min. at twelve temperatures in the range 80 to −70°C. However, when the reduced PBD failure envelope was compared with the reduced SBR envelope, it was found necessary to decrease the measured PBD M_c values by a factor of 1.4 in order to effect superposition. This discrepancy could be due to the use of an inappropriate value of μ, which we took to be 0.44 as reported by Trick (4); his samples had a different cis-trans-vinyl composition than ours so that

the use of his value of μ is questionable. A slightly smaller value of this parameter would bring the experimental results into accord. The high temperature stress-strain curves for the two rubbers are very nearly the same, which would also indicate that the M_c's calculated for PBD using $\mu = 0.44$ are too high.

Thus, it can be concluded that the relative concentration of network chains in samples of a given rubber type can be rapidly and conveniently determined by testing multiple samples at one rate and a suitable temperature. The vertical separation of the curves corresponds then to the logarithm of the relative concentration of chains. If the concentration is known for one sample, the values for the other samples can be determined absolutely. The temperature should be high enough to give breaking strains less than about 300%. Conversely, a portion of the reduced failure envelope can be generated by testing multiple samples of a polymer having varying crosslink densities at one rate and one temperature.

The swelling technique has been used here to obtain the M_c values. However, it would be anticipated that M_c values obtained from "equilibrium" modulus measurements would also be suitable for the purpose.

The effect of M_c on strength is usually given in terms of the familiar σ_b versus ν_e plots, which are characterized by the occurrence of a maximum in σ_b at low ν_e. However this maximum, which is time dependent (3,7), is an artifact caused by the relative rates at which σ_b and ϵ_b change with M_c. When such data are plotted as a reduced failure curve, log $(\sigma_b g/\nu_e)$ versus log ϵ_b, this maximum disappears. In addition, according to the data of Bueche and Dudek, the reduced failure curve representation of σ_b, ν_e data is time independent over the range of strain rates covered.

The range of M_c values investigated here provides a satisfactory check on the theory. However, it would be desirable to be able to report reduced failure envelope data for samples having greater variations in M_c. Work is currently in progress to obtain the data. Literature data do not provide a suitable check on the theory since they suffer from one or more of the following defects: (1) insufficient data available to assess the failure envelope, (2) M_c not varied widely enough, and (3) M_c not reported or determined. However, semiquantitative agreement with theory is provided on SBR by the data of Bueche and Dudek (3) and by Epstein and Smith (5) and on an epoxy resin well above T_g by the data of Kaelble (6).

This paper represents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Advanced Research Projects Agency Letter Order No. 107-62, for the National Aeronautics and Space Administration.

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AN EVIDENCE OF THE HYDROGEN TRANSFER POLYMERIZATION OF METHYL VINYL KETONE

In the alkoxide-catalyzed polymerization of acrylamide and methacrylamide, it is known that specific hydrogen transfer polymerization occurs (1) instead of the usual vinyl polymerization. We should expect that in methyl vinyl ketone the hydrogen of the methyl group adjacent to a carbonyl group would be active and easily move, resulting in hydrogen transfer polymerization, particularly when basic catalysts are used.

Methyl vinyl ketone was polymerized with alkali alkoxide, which is a preferred catalyst in the hydrogen transfer polymerization of acrylamide and methacrylamide. The carbonyl groups of the polymer were converted into acid amide groups by the Schmidt reaction and hydrolyzed with acid. The hydrolyzed product was analyzed using chromatography, and γ-aminobutyric acid was found in the product. From this we conclude that hydrogen transfer polymerization participates in the polymerization of methyl vinyl ketone.

Experiments

(1) Monomer: Methyl vinyl ketone was prepared by the dehydration of γ-ketobutanol which was made from acetone and formaldehyde (2).

(2) Polymerization: The catalyst was sodium tert-butoxide (1×10^{-2} mole/mole of monomer). The solvent was toluene (equal weight to monomer). The inhibitor of the radical polymerization was phenyl-β-naphthylamine (1×10^{-3} g./g. of monomer).

Procedure: 5 g. of methyl vinyl ketone dried over calcium chloride was transferred into an ampoule with catalyst, solvent, and inhibitor using the vacuum line technique. The polymerization was carried out at 0°C. for 50 hr. After the polymerization the product mixture was poured into acetone and stirred well. The acetone soluble part was extracted and precipitated with methanol. The total yield was 2.0977 g. of polymer (acetone soluble part, 2.0937 g.; acetone insoluble part, 0.0040 g.). The reduced viscosity (η_{sp}/c) of the acetone soluble part in methyl ethyl ketone solution was 0.012 at 2 g./l., 30°C. Figure 1 shows the IR spectrum of the acetone soluble polymer.

(3) Schmidt reactions (3): 1 g. of acetone soluble polymer, 50 ml. of chloroform, 20 ml. of concentrated sulfuric acid, and 2 ml. of fuming sulfuric acid were placed in a three-necked flask equipped with a stirrer and air condenser. The vessel was maintained at 35–45°C. with stirring. 1 g. of sodium azide was added during 15 min. and reacted for 2.5 hr. After an additional 45 min. of reaction time with another 0.5 g. of

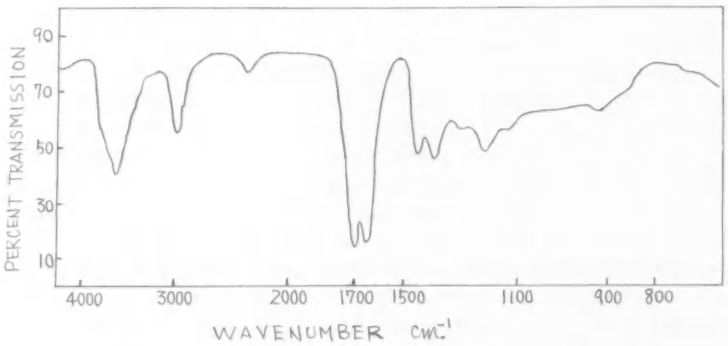


Fig. 1. IR spectrum of acetone soluble polymer of methyl vinyl ketone.

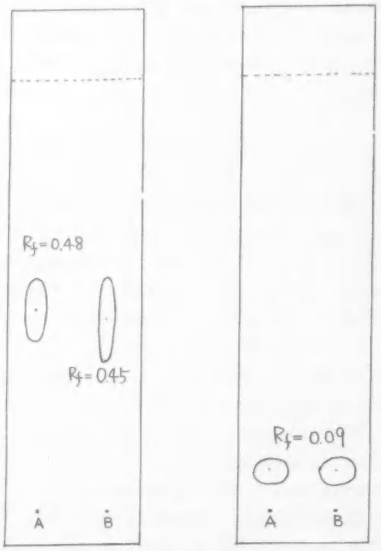


Fig. 2. Paper chromatograms of product A and commercial γ-aminobutyric acid. A: Start points of commercial γ-aminobutyric acid; B: start points of product A. (Left): developer used 4:1 mixture of n-butanol and glacial acetic acid. (Right): developer used n-butanol saturated with ammonia.

sodium azide, the air condenser was removed, and chloroform and excess hydrogen azide were distilled off under reduced pressure. The residual solution was poured onto blocks of ice. The solid part was filtered, washed with water till the sample became free of sulfuric acid, and then

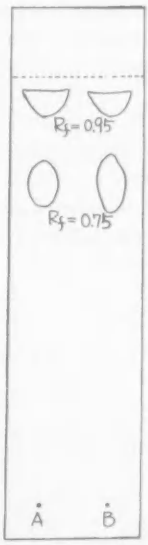


Fig. 3. Paper chromatograms of N-dinitrophenyl derivatives of commercial γ-aminobutyric acid and product A. A: Start point of N-dinitrophenyl γ-aminobutyric acid; B: start point of product A. Developer used n-butanol saturated with ammonia. Upper spots are considered as dinitrophenol; lower spots as N-dinitrophenyl-γ-aminobutyric acid.

dried. The yield was 0.6 g.

(4) Hydrolysis: 0.5 g. of the Schmidt reaction product was hydrolyzed with constant boiling (20%) hydrochloric acid (4). The hydrolyzed product was filtered and the filtrate was dried under vacuum. A small quantity of colored crystalline material was obtained (product A).

(5) Paper chromatography: Product A was compared with a commercial γ-aminobutyric acid by the usual method of chromatography for amino acids (4). Both samples were developed on No. 50 Toyo Filter Paper for chromatography with a 4:1 mixture of n-butanol and glacial acetic acid and also with n-butanol saturated with ammonia (ninhydrin was used for coloring the spots). In both cases, spots appeared at the same height. Figure 2 shows these paper chromatograms.

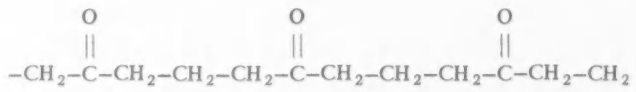
(6) Confirmation by the dinitrophenylamino acid derivatives: According to the usual method (5) product A as well as the commercial γ-aminobutyric acid was reacted with dinitrofluorobenzene in the dark and the resulting yellow products were compared by paper chromatography using n-butanol saturated with ammonia as developer. Four yellow spots were observed at the two same heights, as shown in Figure 3. When dinitrophenol was removed from the N-dinitrophenyl γ-aminobutyric acid by

sublimation, the upper spot disappeared. Therefore, the lower spots are considered to be those of pure N-dinitrophenyl-γ-aminobutyric acid.

From the analysis described above, we may safely conclude that the product A obtained from the methyl vinyl ketone polymer is γ-aminobutyric acid.

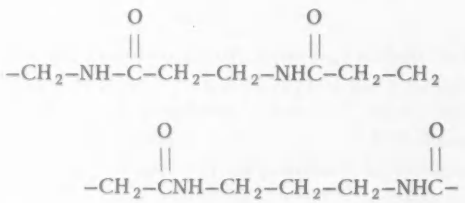
Discussion

If methyl vinyl ketone is polymerized in the hydrogen transfer mechanism, the structure of the polymer must be the following



(I)

By the Schmidt reaction, this polymer is certainly converted into the following structure



(II)

If the polymer of the above structure is hydrolyzed, it is definite that γ-aminobutyric acid, trimethylene diamine, and glutaric acid must be produced. Since γ-aminobutyric acid was found in our hydrolyzed products, it is concluded that at least a part of the polymer has the structure (I) and, hence, that hydrogen transfer polymerization must participate in the polymerization of methyl vinyl ketone with alkoxide catalyst.

Detailed studies on the effects of monomer structure of vinyl ketones, catalyst and solvent on the mechanism of polymerization are now in progress.

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THE ENERGETICS OF THE DEPOLYMERIZATION OF POLY(METHYL METHACRYLATE)

As with radical chain reactions generally, the overall energy of activation for depolymerization is a composite quantity involving the energies of activation of the various constituent reactions. The reaction mechanism for the depolymerization of poly(methyl methacrylate), is firmly established (1) and the overall energies of activation of the thermally and photochemically initiated reactions are given by eqs. (1) and (2) respectively,

$$E_{o,T} = E_d + \frac{1}{2}E_i - \frac{1}{2}E_t \quad (1)$$

$$E_{o,P} = E_d - \frac{1}{2}E_t \quad (2)$$

in which E_d, E_i, and E_t are the energies of activation for depropagation, initiation, and termination.

Since depropagation is the exact reverse of the propagation step in polymerization it is clear that,

$$E_d = E_p - \Delta H \quad (3)$$

in which E_p is the energy of activation for propagation and ΔH is the heat of polymerization.

Normally ΔH is measured calorimetrically using liquid monomer and, using Dainton and Ivin's (2) notation, is written ΔH_{lc}. Polymer degradation reactions involve the condensed and gaseous states, however, so that ΔH in eq. (3) should be represented by ΔH_{gc}. Using Ivin's (3) value of -21.4 kcal./mole for ΔH_{gc}, it can be shown as follows that the energetic results quoted by various authors for the depolymerization of poly(methyl methacrylate) become self-consistent.

Taking a value of 5 kcal./mole for E_p (4), E_d is found to be 26.4 kcal./mole. Thus using Cowley and Melville's value (5) of 8 kcal./mole for $E_{o,P}$, a value of 37 kcal./mole is obtained for E_t. Using $\Delta H_{lc} = 13.5$ kcal./mole, Cowley and Melville (5) had obtained a value of 20 kcal./mole for E_t.

Bywater (6) studied the thermal depolymerization of poly (methyl methacrylate) with terminal hydroxyl groups in the same temperature region as Cowley and Melville and obtained the values 48 and 31 kcal./mole for E_i and $E_{o,T}$, respectively. Using eq. (1) a value of 38 kcal./

mole for E_t may be deduced, which is in excellent agreement with that of Cowley and Melville above.

For the thermal depolymerization of poly(methyl methacrylate) initiated by the breaking of carbon-carbon bonds at random along the polymer chains, Brockhaus and Jenckel (7) found E_o to be 48 kcal./mole. Using the values already quoted for E_d and E_t and applying eq. (1), E_i is found to be about 81 kcal./mole, which is a reasonable value for the dissociation of a C–C bond.

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NEW CATALYST SYSTEMS AND THEIR APPLICATION TO THE POLYMERIZATION OF PHENYLACETYLENE

A number of investigations on the polymerization of phenylacetylene (PA) have been published in the last several years. Heating (1,2), radiation (3), or use of a few common Ziegler-type catalysts (4-6) have been adopted as the initiation method for high polymerization. The polymers obtained by any of these methods have been shown to be of low molecular weight. Among them the last one appears to be most favorable to obtain polymers of higher molecular weight.

The authors (7) could have recently shown, however, that for the high polymerization of PA the triethylaluminum ($AlEt_3$)/metal acetylacetonate catalyst systems are, on the whole, better than common Ziegler-type catalysts. Specifically, $Fe(acac)_3$,* $V(acac)_3$, and $VO(acac)_2$ have been shown to have the best co-catalytic activity when used in combination with $AlEt_3$. So, in order to further study co-catalytic activity of chelate compounds they (8) have attempted the polymerization of PA with various complex catalysts composed of $AlEt_3$ and many chelate compounds other than metal acetylacetonates. Some of the results are shown in Table I.

In this communication the authors report that they found for the first time very interesting catalyst systems, i.e., metal alkyl/metal dimethylglyoximate systems, and that these, particularly $AlEt_3/Fe(dmg)_2$† catalyst, are effective for the high polymerization of PA. At the same time it will also be shown that the transition metal of a Ziegler-type catalyst plays an important role in the polymerization.

In general, the polymerizations were carried out in sealed glass ampoules. Detailed precedure was similar to that described in a previous paper (9). After polymerization, the benzene solution of the resulting polymer was refluxed together with 2N HCl. Then it was washed successively with a 2N solution of HCl in CH_3OH (a 35% solution of HCl in water was diluted to 2N with CH_3OH), water (until neutral), 10% Na_2CO_3, and finally, water again (until neutral). The refined polymer was fractionated at room temperature into three polymers, i.e., a benzene insoluble polymer (I) (orange to crimson bulky matter), a benzene soluble and methanol insoluble polymer (II) (yellow powder), and a methanol soluble polymer (III) (yellow to brownish yellow powder). The number-average molecular weight of the polymer II was measured by using a Mechrolab vapor pressure osmometer.

First, attempts to react $AlEt_3$ with $Ni(dmg)_2$ were made, resulting in

* $Fe(acac)_3$: tris(acetylacetone)iron(III).

† $Fe(dmg)_2$: bis(dimethylglyoximo)iron(II).

TABLE I

Polymerization of Phenylacetylene with Various $AlEt_3$/ Metal Chelate Compound Catalyst Systems [a]

No.	Chelate compound [b]	Molar ratio of $AlEt_3$/ chelate compound	R [c]	Polymn. time, hr.	Polymer yield, %			$\overline{Mn}$ (II) [d] $\times 10^{-3}$
					I	II	III	
1	$Co(oxin)_2$	3	4	50	trace	trace	33.7	–
2	$Co(sal)_2$	2	4	50	0.5	5.1	35.4	–
3	$Ni(saldxm)_2$	3	4	50	0.2	2.9	67.4	–
4	$VO(sal)_2$	3	5	20	3.5	58.3	17.9	7.7
5	$VO(saldim)_2$	3	5	20	1.5	29.7	14.3	2.8
6	$Fe(sal)_3$	3	5	20	2.2	43.4	53.7	6.3

[a] Reaction conditions were as follows: solvent: toluene; catalyst preparation: for 15 min. at 70°C.; amount of chelate compounds: 2 mole % to monomer; polymerization temperature: 30°C.; $AlEt_3$: 1.00N solution prepared by diluting a 2.00N solution of $AlEt_3$ in n-hexane with toluene was used.

[b] Abbreviations are as follows: $Co(oxin)_2$: bis(8-hydroxyquinoline)cabalt(II); $Co(sal)_2$: bis(salicylaldehyde)cobalt(II); $Ni(saldxm)_2$: bis(salicylaldoxime) nickel(II); $VO(saldim)_2$: bis(salicylaldehydeimine)oxovanadium(IV).

[c] R: Volume ratio of ($AlEt_3$ solution + solvent)/monomer.

[d] $\overline{Mn}$ (II): Number-average molecular weight of the polymer II.

TABLE II

Polymerization of Phenylacetylene with the Metal Alkyl/ Metal Dimethylglyoximate Catalyst Systems [a]

No.	Metal alkyl	Metal dimethyl-glyoximate	R [e]	Polymn. time hr.	Polymer yield, %			$\overline{Mn}$ (II) [f] $\times 10^{-3}$
					I	II	III	
7	$AlEt_3$ [b]	$Ni(dmg)_2$	4	50	trace	0.5	25.7	–
8	$AlEt_3$	$Co(dmg)_3$	4	50	0.3	3.4	12.7	3.6
9	$AlEt_3$	$Fe(dmg)_2 \cdot 2Py$	5	20	0.8	10.4	18.1	5.7
10	$AlEt_3$	$Fe(dmg)_2 \cdot 2NH_3$	5	20	0.1	4.0	18.6	6.1
11	$AlEt_3$	$Fe(dmg)_2$ [d]	5	20	51.8	39.7	9	8.0
12	$AlEt_2Cl$ [c]	$Fe(dmg)_2$ [d]	5	20	0	0	2.0	–

[a] Reaction conditions were as follows: solvent: toluene; catalyst preparation: for 15 min. at 70°C.; molar ratio of metal alkyl/metal dimethylglyoximate: 3; amount of chelate compounds: 2 mole % to monomer; polymerization temperature: 30°C.

[b] A 1.00N solution of $AlEt_3$ was used, prepared by diluting a 2.00N solution in n-hexane with toluene.

[c] A 1.00N solution of $AlEt_2Cl$ in n-hexane was used.

[d] Calculated amount of $Fe(dmg)_2 \cdot 2NH_3$ (6 mole % to monomer) was heated for 2 hr. at 130–140°C. under a reduced pressure of ca. 10^{-4} mm. Hg.

[e] R: Volume ratio of (metal alkyl solution + solvent)/monomer.

[f] $\overline{Mn}$ (II): Number-average molecular weight of the polymer II.

formation of a reddish dark brown complex at 70°C. or above in an aliphatic or aromatic hydrocarbon. Phenylacetylene could indeed be polymerized with this catalyst in low yield of the polymer II, indicating that it is not highly effective for the high polymerization (No. 7). An analogous, but a slightly better, result was obtained by using the $AlEt_3$/ $Co(dmg)_3$ complex catalyst (No. 8).

In view of the fact that in the high polymerization of PA, $Fe(acac)_3$ has far better co-catalytic activity in combination with $AlEt_3$ than $Ni(acac)_2$ or $Co(acac)_3$, the authors deduced that the $AlEt_3$/ $Fe(dmg)_2$ system would be one of the best catalysts for the polymerization. Therefore, the following experiments were carried out.

Since $Fe(dmg)_2$ has not been isolated because of its unstability (10, 11), the authors synthesized first $Fe(dmg)_2 \cdot 2Py$ (Py: pyridine) (reddish brown crystal) by the method similar to Tschugaeff's (10). Similarly $Fe(dmg)_2 \cdot 2NH_3$ (purplish red crystal) was prepared. Phenylacetylene was polymerized slowly by either the $AlEt_3/Fe(dmg)_2 \cdot 2Py$ or the $AlEt_3/Fe(dmg)_2 \cdot 2NH_3$ catalyst (Nos. 9 and 10).

Then, $Fe(dmg)_2 \cdot 2NH_3$ was heated at 130–140°C. for 2 hr. under a reduced pressure of about 10^{-4} mm. Hg to remove ammonia. The residual crystal, probably $Fe(dmg)_2$, was allowed to react with $AlEt_3$ to give a purplish dark brown complex. It could polymerize the monomer, as was inferred, at a surprisingly rapid reaction rate, and the reaction mixture turned almost instantly to a gel (No. 11). In this case it may be noted that the yield of the polymer I is remarkably high, and such a high yield of this polymer has never been reached by using other catalysts under comparable conditions. In general, those catalysts that give a large yield of polymer I under the same conditions have been known (7,8) to be more effective for the high polymerization of PA than those that do not. Hence, the authors believe that this catalyst would be the most effective one in giving high molecular weight polymers of PA. On the other hand, the complex catalyst derived from $AlEt_2Cl$ and the residual crystal, presumably $Fe(dmg)_2$, could hardly polymerize the monomer.

The above results are summarized in Table II.

The results obtained using the $AlEt_3$/iron chelate compound complex catalysts seem to be explained either (1) by assuming that even after the complex catalysts were formed, ammonia or pyridine molecules would be coordinated to the iron atom, so that the donor molecules would prevent the coordination of the monomer onto the iron atom, or (2) by assuming that such effective catalyst species as were formed by reaction of $AlEt_3$ with the residual crystal (No. 11) would be able to exist only in small quantities at lower molar ratios of $AlEt_3/Fe(dmg)_2 \cdot 2D$ (D: donor molecule) since the $AlEt_3$ added would be consumed in its reaction with D's. In these assumptions, activation of the monomer on the transition metal is supposed to be indispensable as the first step of polymerization, whatever the next step may be. In case of the former assumption

TABLE III

Polymerization of Phenylacetylene with the $AlEt_3/Fe(dmg)_2 \cdot 2Py$ Catalyst System [a]

No.	Molar ratio of $AlEt_3$ to $Fe(dmg)_2 \cdot 2Py$	Polymer yield, %			$\overline{Mn}$ (II) [b] $\times 10^{-3}$
		I	II	III	
13	2.10	0	0	0.5	–
14	4.20	0.2	3.0	2.3	4.0
15	5.25	2.4	5.2	4.8	3.7
16	6.30	4.1	15.8	6.4	8.0
17	8.39	32.2	20.8	14.0	4.5
18	9.44	38.4	37.2	14.1	7.8
19	10.49	22.0	48.5	20.9	5.1
20	11.54	4.4	34.3	15.5	8.9
21	12.59	1.4	16.5	12.4	6.5
22	15.73	trace	6.1	11.3	3.8

[a] Reaction conditions were as follows: solvent: toluene; catalyst preparation: for 15 min. at 90°C.; amount of $Fe(dmg)_2 \cdot 2Py$: 1 mole % to monomer; polymerization temperature: 30°C.; polymerization time: 1.0 hr.; volume ratio of ($AlEt_3$ solution + solvent)/monomer: 5; $AlEt_3$: toluene solution was used.

[b] $\overline{Mn}$ (II): Number-average molecular weight of the polymer II.

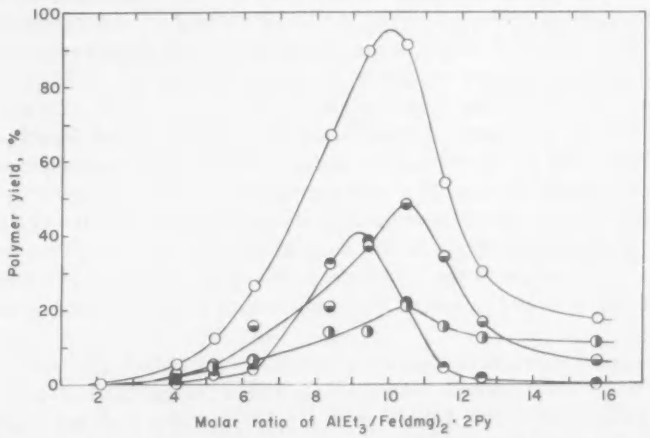

Fig. 1. Effect of the molar ratio of $AlEt_3/Fe(dmg)_2 \cdot 2Py$ on the polymer yields. (–○–) Total polymer yield; (–◓–) yield of the polymer I; (–◒–) yield of the polymer II; (–◑–) yield of the polymer III.

the occurrence of exchange between donor molecules and the monomer might be approved, since some degree of polymerization has really occurred when catalysts derived from $AlEt_3$ and $Fe(dmg)_2 \cdot 2D$ were used. For these suppositions additional description will be given below. On the basis of either of these concepts the decreasing co-catalytic activity of these iron chelate compounds should be of the following order,

$$Fe(dmg)_2 \gg Fe(dmg)_2 \cdot 2Py > Fe(dmg)_2 \cdot 2NH_3$$

because the first one is considered to have the strongest and incomparable activity for lack of donor molecules, and the coordination power of Py has been shown to be weaker than that of NH_3 (12). This trend of co-catalytic activity is in good agreement with the experimental results.

Since it has been shown that $AlEt_3$ can react with various compounds having a lone pair or lone pairs of electrons to form stable compounds, free and excess $AlEt_3$ in the polymerization systems catalyzed by the $AlEt_3/Fe(dmg)_2 \cdot 2D$ complex is considered to be able to pull out the donor molecules in the chelate compound or in the complex catalyst as stated in assumption (1). Thus, the $Fe(dmg)_2$ formed would react with $AlEt_3$ to give the most effective catalyst (No. 11). Experimental confirmation for this is shown in Table III and Figure 1. The rate of polymerization was found to increase steadily as the molar ratio of $AlEt_3/Fe(dmg)_2 \cdot 2Py$ was increased up to values near 10, and then declined. The former fact is considered to be due to the catalytic action of the $AlEt_3/Fe(dmg)_2$ catalyst, and the latter may be attributed to inhibition action of $AlEt_3$ or $Py \cdot AlEt_3$. It may be noted from Figure 1 that the maximum yields of the polymers I and II were obtained at different ratios. The molecular weight of the polymer II did not change regularly with the molar ratio.

It was then clear that regarding chelate compounds of Fe, Co, and Ni, the orders of co-catalytic activities are the same, independent of ligand structures, and that the donor molecules coordinated to the transition metal of a metal dimethylglyoximate remarkably reduce its co-catalytic activity. These results seem to strongly support the inference (7,8) that in the high polymerization of any monosubstituted acetylene, coordination of the monomer or the polymer onto the transition metal of a Ziegler-type catalyst would be one of important factors in each component reaction.

The metal alkyl/metal dimethylglyoximate complex catalysts discovered by the present authors have been applied to the polymerization of epoxides by one of the authors et al. (13,14) to obtain high molecular weight and highly crystalline polymers. Studies are continuing in order to define the high activity of this type of catalyst, and to determine the structures of the complex catalysts.

Further studies are currently under way, and more detailed results and discussion will be published in the near future.

The authors wish to express their thanks to Mitsui Chemical Industries Co. Ltd. for the supply of triethylaluminum.

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CARBON DISULFIDE-INSOLUBLE SULFUR*

In order to prevent additional misunderstanding concerning the subject of our note (1) entitled "On the Structure of Carbon Disulfide-Insoluble Sulfur" we wish to emphasize that that note was concerned only with a particular helical structure proposed by Pinkus et al. (2,3) on the basis of data reported by them (4) for a preparation of carbon disulfide-insoluble sulfur made by slow cooling of a sulfur melt. Our note showed that this preparation was in fact ordinary orthorhombic sulfur, and that the proposed helical structure (2,3) was accordingly unacceptable. We did not mean to imply, as has since been inferred (5), that other preparations of carbon disulfide-insoluble sulfur were not helical in nature. X-ray diffraction data from carbon disulfide-insoluble (fibrous) sulfur prepared by quick quenching of liquid sulfur (5,6) are completely different from those reported by Pinkus et al., and have been attributed (5-7) to a helical structure, although the conventional proof has yet to be published. Our point is that the data of Pinkus et al. do not pertain to a helical structure, and not that "carbon disulfide-insoluble sulfur," of whatever other origin, is not helical.

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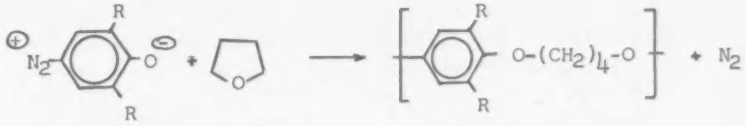
PHENYL ETHER COPOLYMERS: COPOLYMERIZATION OF DIAZOOXIDES WITH CYCLIC ETHERS

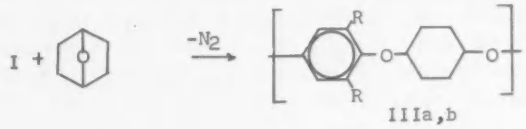
We had reported earlier (1) that the diazooxides p-benzoquinone diazide (Ia) and 2,6-dimethyl-p-benzoquinone diazide (Ib) would decompose in a tetrahydrofuran solvent under the influence of heat or light to give 1 : 1 copolymers (II) with the solvent.



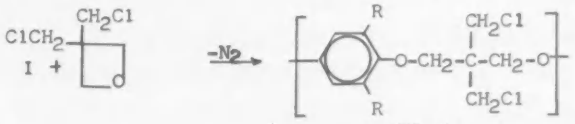
Ia, R=H
b, R=CH_3

IIa, R=H
b, R=CH_3

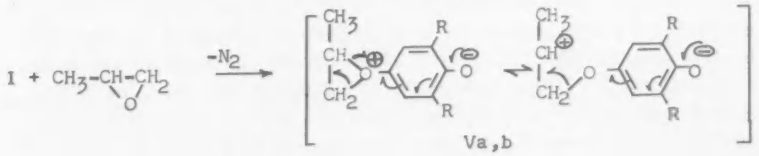
On the basis of the behavior of the diazooxides in this and other solvents, and on the basis of the known reactions of furans with cationic and radical reagents, a cationic mechanism which afforded an alternating copolymer was postulated. We had predicted that the p-benzoqui-



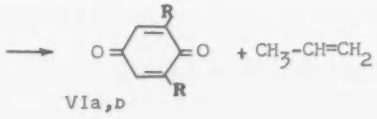
IIIa,b



IVa,b



Va,b



VIa,b

a, R=H
b, R=CH_3

TABLE I

Copolymerization of Diazooxides with Cyclic Ethers

Polymer	Conversion, %	Molecular Weight [a]	Solubility, % [b]
IIa	75	3000-6000	100
IIb	45	2200-2500	100
IIIa	85	2200-3000	35
IIIb	62	2500-2800	100
IVa	7	4520	80
IVb	trace	–	–

[a] Molecular weights were obtained in chloroform on a Mechrolab 301 A vapor pressure osmometer.

[b] In chloroform.

TABLE II

Analytical Data on Copolymers

Polymer	Combustion analysis, % C		NMR analysis, proton ratio, aromatic : aliphatic	
	Calcd.	Found	Calcd.	Found
IIa	73.15	72.44	4 : 8	4 : 8
IIb	74.97	73.95	2 : 14	2 : 14.7
IIIa	75.80	73.40	4 : 10	4 : 10.3
IIIb	77.10	77.37	2 : 16	2 : 15.4
IVa	–	–	4 : 8	4 : 8

none diazides would copolymerize with other monomeric Lewis bases which would undergo ring-opening polymerization reactions by cationic catalysts.

Three other cyclic ethers, 1,4-epoxycyclohexane, 3,3-bis-chloromethyl oxetane, and propylene oxide, were chosen for study. 1,4-Epoxycyclohexane provided good yields of polymer (III) of about the same molecular weight (2000-3000) as was obtained with the tetrahydrofuran comonomer (Table I). Very low yields of copolymer with 3,3-bis-chloromethyl oxetane (IV) were obtained. Surprisingly enough, propylene oxide, which demonstrates the greatest propensity to polymerize under cationic conditions compared to the other cyclic ethers, did not form copolymer but was reduced by the diazooxides in the formation of p-benzoquinones (VI).

The intermediate Lewis salt (V), which is of the type postulated in the mechanism of the ring opening polymerization of the other cyclic ethers

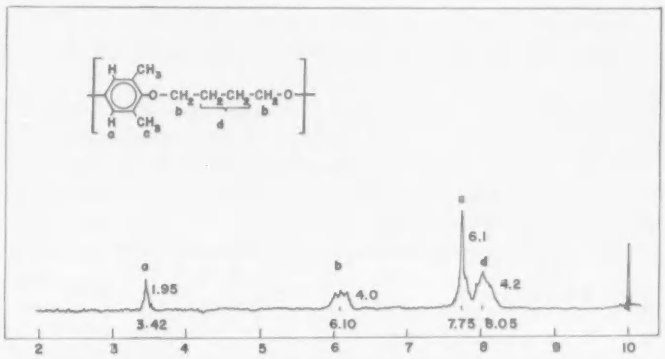


Fig. 1. NMR spectrum of a 2,6-dimethyl-p-benzoquinone diazide – tetrahydrofuran copolymer.

(1), has two convenient paths available for product formation and evidently does not choose the ring opening polymerization. The higher membered cyclic ethers, oxetanes, and furans, do not have the alternate path available and must react by ring opening to afford polymer.

Further evidence for the 1 : 1 stoichiometry in the copolymer formed from tetrahydrofuran and 2,6-dimethyl-p-benzoquinone diazide had been obtained by a study of the NMR spectrum (2). The analytical results on the copolymers are presented in Table II. The NMR spectra of the polymers offer a particularly convenient mode of copolymer analysis, since the position of the aromatic protons associated only with the phenyl ether comonomer is cleanly down field. An example of the NMR spectrum of the 2,6-dimethyl-p-benzoquinone diazide copolymer with tetrahydrofuran (Fig. 1) clearly demonstrates the utility of this mode of analysis.

We wish to thank the Research Department, Hercules Powder Company for their generous gift of the monomer 3,3-bis-chloromethyl oxetane.

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POLYMER LETTERS VOL. 1, PP. 567-570 (1963)

CARBON MONOXIDE – FORMALDEHYDE COPOLYMERS

The acetal polymers, especially high molecular weight polyformaldehyde, have received considerable attention within recent years and some reviews have lately shown the development in this field (1,2).

Copolymers of formaldehyde with other aldehydes (3,4), cyclic ethers (5), isocyanates (6), isocyanic acid (7), lactones (8), cyclic anhydrides (9), and some monomers containing carbon-carbon double bond (10-13) are also reported.

Carbon monoxide homopolymers have never been described; only copolymers with ethylene or olefins have been prepared (14). We have studied the high molecular weight products obtained from formaldehyde and carbon monoxide. Carbon monoxide reacts with aqueous formaldehyde yielding glycolic acid (15). We have found that the reaction of carbon monoxide with anhydrous formaldehyde in the presence of a Lewis-acid gives polymers having ester, ether, and acetal groups in the chain. Mass balance and elemental analysis show that carbon monoxide reacts with formaldehyde and the molar ratio CO/CH_2O in the polymers can reach 1 as maximum value.

Ammonolysis of the products having a molar ratio $CO/CH_2O < 1$ (A) gives glycolamide, diglycolamide, and hexamethylenetetramine. Ammonolysis of the products having a molar ratio CO/CH_2O about 1 (B) gives glycolamide, diglycolamide, and traces of hexamethylenetetramine. These results show that the chain of the (A) polymer contains the structural units (a), (b), and (c)

$$-CO-CH_2-O- \qquad (a)$$

$$-CO-CH_2-O-CH_2-CO-O- \qquad (b)$$

$$-CH_2-O- \qquad (c)$$

and (B) polymer contains almost exclusively the structural units (a) and (b).

Infrared spectra of the products are in good agreement with these results. Infrared spectrum of (B) (Fig. 1) is quite similar to that one of polyglycolic acid (Fig. 2), both having the fundamental bands assignable to ester groups. In the infrared spectrum of polyglycolic acid the 1750 $cm.^{-1}$ band is characteristic of stretching vibration of C = O ester group and the band at about 1215 $cm.^{-1}$ is characteristic of stretching vibration of C – O ester group. Both of these bands are broad and their shape depends on the physical state of the sample. The 1092 $cm.^{-1}$

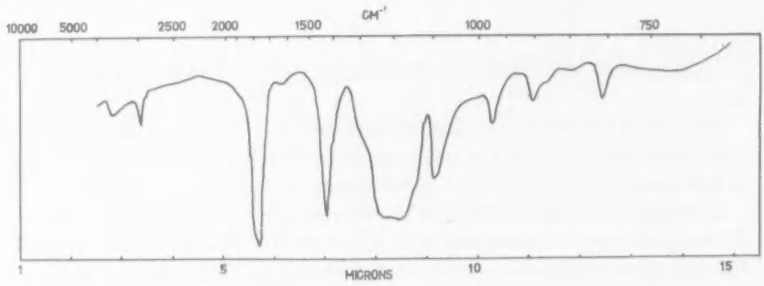

Fig. 1. Infrared spectrum of a copolymer having a molar ratio $CO/CH_2 \simeq 1$ (B).

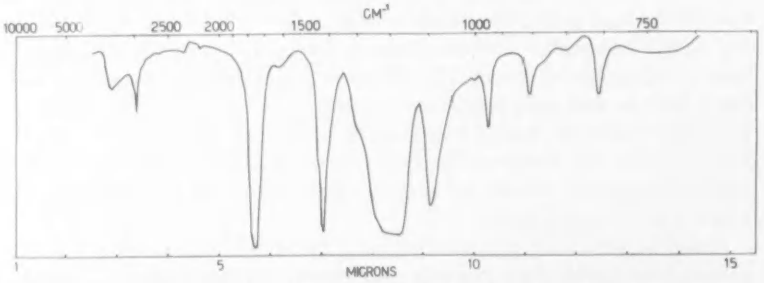

Fig. 2. Infrared spectrum of polyglycolic acid.

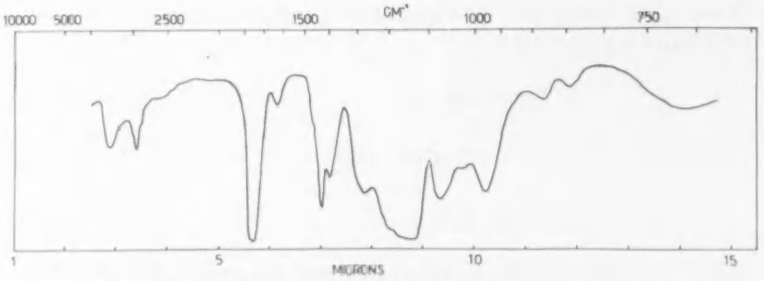

Fig. 3. Infrared spectrum of a copolymer having a molar ratio $CO/CH_2O < 1$ (A).

band can be assigned to the stretching vibration of $CH_2 - O$ group, and the 1420 cm.$^{-1}$ band can be assigned to the bending vibration of $- CH_2$ group. The same bands are present in (B) spectrum with only slight differences. The most important difference is the presence of a weak band at 1140 cm.$^{-1}$, as a shoulder of the 1215 cm.$^{-1}$ band, assignable to the stretching vibration of $C - O - C$ ether group. Also the infrared spectrum of (A) (Fig. 3) has ν (C = O) at about 1755 cm.$^{-1}$ and $\delta(CH_2)$ at

about 1425 cm.$^{-1}$, and is more complicated in the 1250 – 950 cm.$^{-1}$ region than that of the (B) spectrum. The absorbance in the 1200 cm.$^{-1}$ region is assignable chiefly to ν(C – O) of glycolic and diglycolic ester groups, and the 1135 cm.$^{-1}$ band to ν(C – O) of diglycolic ether groups. The absorbance in the 1080 – 950 cm.$^{-1}$ region receives some contribution from the ν (C – O) acetal units.

The polymers are easily hydrolysable and chemical analysis of – OH and – COOH end groups was not possible. The determination of – – OCH_3 groups indicates that very few are present.

The molecular structure of carbon monoxide (16) and the catalyst used suggests a cationic polymerization. The mechanism might involve the following steps:

$$\sim\!\!\sim - O - \overset{+}{C}H_2 + O = CH_2 \rightleftharpoons \sim\!\!\sim - O - CH_2 - O - \overset{+}{C}H_2 \qquad (1)$$

$$\sim\!\!\sim - O - \overset{+}{C}H_2 + CO \longrightarrow \sim\!\!\sim - O - CH_2 - \overset{O}{\overset{\|}{C}}{}^{+} \qquad (2)$$

$$\sim\!\!\sim - O - CH_2 - \overset{O}{\overset{\|}{C}}{}^{+} + O = CH_2 \longrightarrow \sim\!\!\sim - O - CH_2 - CO - O - \overset{+}{C}H_2 \qquad (3)$$

The structural units – CO – CH_2 – O – CH_2 – CO – O might be formed by the insertion reaction (17):

$$\sim\!\!\sim - O - CH_2 - O - CH_2 - O - CH_2 - CO - O - CH_2 - \sim\!\!\sim + CO \longrightarrow$$

$$\longrightarrow \sim\!\!\sim - O - CH_2 - O - CO - CH_2 - O - CH_2 - CO - O - CH_2 - \sim\!\!\sim \qquad (4)$$

The maximum probability for the formation of (b) units occurs when the reaction (4) involves a chain – $(O - CH_2)_n$ – CO – having n = 3.

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SPHERULITE DEFORMATION IN POLYBUTENE-1*

In previous publications (1,2), it was shown that the change in birefringence with elongation of polybutene-1 and polypropylene depends upon the time after preparation of a quenched sample. The strain-optical coefficient at small strains for a freshly-quenched sample is positive while that for an aged sample is negative. A theory for this was proposed (2,3) in which the negative birefringence is attributed to the affine deformation of the spherulite with preservation of the crystal orientation within the spherulite, while the positive birefringence is associated with a re-orientation of the crystals accompanying deformation. Upon aging, the mobility of the crystals within the spherulite is reduced.

The postulate of spherulite deformation has now been verified by direct microscopic observation. Films of polybutene-1, about 1 mil thickness, (made from samples obtained through the courtesy of Phillips Petroleum Company) were prepared by molding in a laboratory press at 150°C. for 15 min. at 2,000 p.s.i. pressure and then lowering the temperature to less than 80°C. at the natural cooling rate of the press before removing. They were stretched varying amounts, either directly after preparation or after aging, for more than 100 hr. No changes in spherulite appearance or birefringence was detectable upon aging, even though the crystal structure is known to change during this period (1,4,5). However, the changes of the birefringence of the spherulites of the fresh and

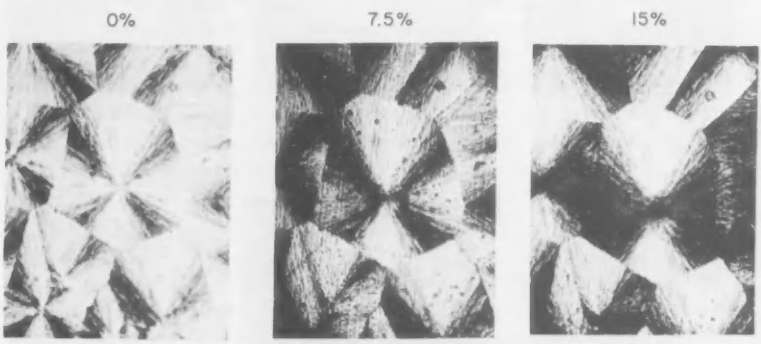

Fig. 1. The change in the appearance of the spherulites of an aged polybutene-1 sample upon stretching. The stretching direction is vertical and the polarizer and analyzer are at ± 45°. Per cent elongations are indicated.

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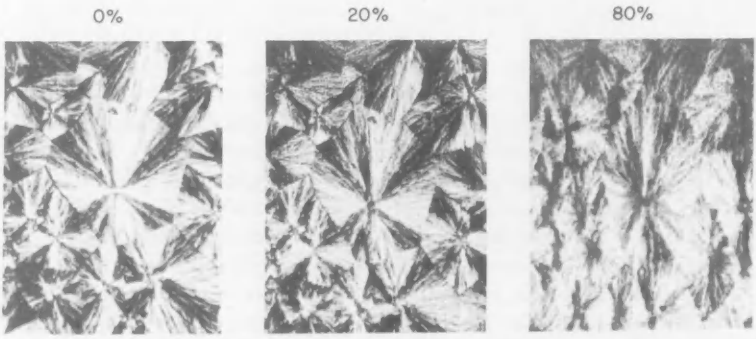

Fig. 2. The change in the appearance of the spherulites of a fresh polybutene-1 sample upon stretching.

aged samples upon stretching are different (Figs. 1 & 2). It is apparent that the spherulite structure undergoes an affine deformation, the dimensions of the spherulite transforming approximately as do the external dimensions of the sample in both cases. The birefringence of the aged spherulite is much more sensitive to deformation and changes percep-

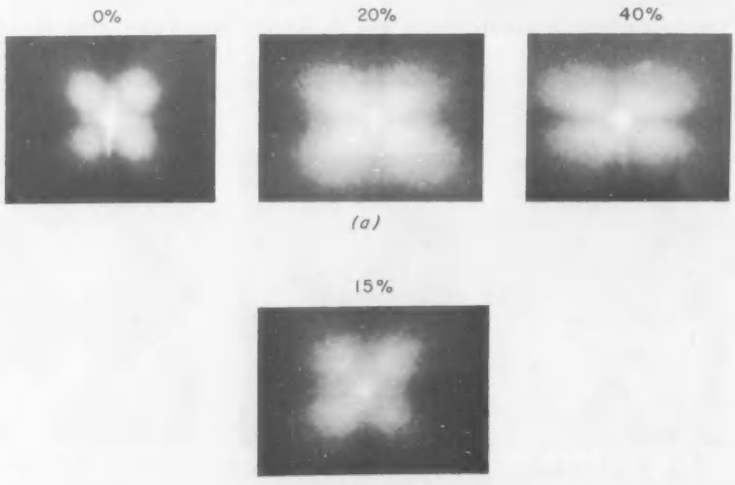

Fig. 3. The H_v light scattering photographs for undeformed and stretched samples of (a) fresh and (b) aged polybutene-1. The stretching direction is vertical and the polarization directions are horizontal and vertical. Per cent elongations are indicated. The 0% elongation figure is identical for fresh and aged samples.

tibly for less than 7 1/2% elongation of the sample, while comparable birefringence changes do not take place until 10-20% elongation for the fresh sample. This is probably a consequence of the lower mobility of the crystals within the aged spherulites.

The maltese extinction cross of the spherulite is oriented parallel to the polarizer and analyzer in the unstretched state. For the aged spherulites, Figure 1 shows an increase in the bright area of the spherulite in the polar regions (in the stretching direction) and a darkening in the equatorial regions, while for the fresh spherulites, Figure 2, the darkening occurs in the polar regions. Examination of interference colors, using a first-order red plate, indicates that the spherulite birefringence is initially negative and becomes more negative in the polar regions on deforming, but the reverse occurs for the fresh spherulites. This is consistent with the postulate of the theory and indicates that the reversal in the sign of the macroscopic strain-optical coefficient upon aging is associated with a reversal in sign of the change in birefringence of the spherulite upon deformation.

Since the reversal in sign of the strain-optical coefficient of the sample has been associated with a change in the mode of crystal orientation in the sample, from that of the b- to the c-axis orienting parallel to the stretching direction (1), it would appear that the present results indicate that it is the change of crystal orientation within the spherulite upon deformation which changes upon aging as has been proposed (1-3). It would agree with the assumption that the b-axis remains radial for the aged spherulite but that recrystallization results in the c-axis becoming radially oriented upon deforming spherulites in a fresh sample.

H_v light scattering patterns for the undeformed and stretched samples of both forms of polybutene-1 are given in Figure 3. The deformation of the pattern associated with the spherulite deformation (6) is readily observable for the fresh sample but not for the aged.

It is believed that texture changes upon stretching crystalline polymers are, in general, related to the deformation of the spherulites, fibrils, or other aggregates within which the crystals reside.

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Amherst, Massachusetts

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*On leave from The Asahi Chemical Company, Japan.

ERRATA

THE STEREOREGULARITY OF TRIMETHYL LEVOGLUCOSAN POLYMERIZATION

(J. Polymer Sci., B1, 163-165, 1963)

By CHEN-CHUAN TU and CONRAD SCHUERCH, Department of Chemistry, State University College of Forestry, Syracuse University, Syracuse, New York

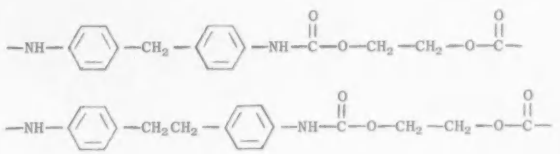
On page 165, line 1 should read: "polymerization of vinyl ethers described by Schildknecht."

MEASUREMENT OF GLASS TRANSITION TEMPERATURES OF POLYMERS BY A DIFFERENTIAL PRESSURE TRANSDUCER

(J. Polymer Sci., B1, 317-321, 1963)

By JORGE HELLER and DONALD J. LYMAN, Stanford Research Institute, Menlo Park, California

On page 320, the structures shown should read as follows:



POLYMER NEWS

A Polymer Colloquium on the subject of "Reactivity of Monomers in Copolymerization" will be held as part of the Annual Chemistry Conference sponsored by the Kansas City Section of the American Chemical Society on November 15, 1963, at the University of Kansas City (now the University of Missouri at Kansas City). The Colloquium will be held in the Linda Hall Library auditorium, 5109 Cherry Street, Kansas City, Missouri. The program as presently constituted, subject to possible additions, is as follows: "General Monomer Reactivity in Binary and Ternary Polymerizations," George E. Ham, Spencer Chemical Co., Research Center, Merriam, Kansas; "The Q-e Scheme, its Use and Abuse," Lewis J. Young, Dow Chemical Company, Midland, Michigan; "Reactivity Ratios of Model Ethylene Copolymerizations and Their Use in Q-e Calculations," Nathan L. Zutty, R. D. Burkhart, Union Carbide & Chemical, S. Charleston, W. Va.; "Three-Component Copolymerization Patterns," R. J. Slocombe, Monsanto Chemical Co., St. Louis, Missouri; "Some New Studies on the Reactivity of Ethylene with Polar Monomers," George E. Ham, Francis E. Brown, Spencer Chemical Co., Merriam, Kansas.

For further information please write Dr. George E. Ham, Spencer Chemical Research Center, 9009 West 67th Street, Merriam, Kansas.

Manuscripts should be submitted to one of the members of the Editorial Board or to the Editorial Office, c/o H. Mark, Polytechnic Institute of Brooklyn, 333 Jay Street, Brooklyn 1, New York. Address all other correspondence to Interscience Publishers, a Division of John Wiley & Sons, Inc., 605 Third Avenue, New York 16, New York.